PATENT SPECIFICATION

(11) 1330 100

NO DRAWINGS

(21) Application No. 23056/72 (22) Filed 17 May 1972

(31) Convention Application No. 157625 (32) Filed 28 June 1971 in

(33) United States of America (US)

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C3B 1C10 1C25 1D2B 1D2C 1L2X 1L6G 1N4G 1N6A 1N6D1 1N6D5 1N6D8 1T1A

G2C C15

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(19)

(72) Inventors MICHAEL JAMES CANESTRARO and MICHALE THEODORE ORINIK

(54) AN EPOXY RESIN COMPOSITION

(71) We, INTERNATIONAL BUSINESS MACHINES CORPORATION, a Corporation organized and existing ...

anhydride, and a halogenated hydrocarbon solvent.

ERRATUM

SPECIFICATION No. 1,330,100

Page 3, line 15, *for* 8000 *read* 800

THE PATENT OFFICE
10th October, 1973

... material which, upon exposure to light, will become soluble to a given solvent in the exposed areas while insoluble in the unexposed areas, i.e. a positive resist material. It is desirable that this material also be a good dielectric material so that a subsequent circuit can be disposed thereon without need of the conventional steps of removing the photoresist material and coating the circuitry board with a dielectric.

While there are a number of commercially available positive photoresist compositions, such as Shipley's AZ-1350, AZ-119, Eastman Kodak KAR-3, none of these materials are found to be suitable dielectric materials in the preparation of printed circuitry.

According to the invention there is provided an epoxy resin composiiton comprising an epoxy resin having an epoxide equivalent weight of from 800 to 2000; an amine curing agent; a halogenated polycarboxylic acid ...

holes for interconnecting metallic layers, one can use an appropriate mask and "dissolve out" the hole with mild organic solvents, and then follow with conventional electroless and metal plate through techniques to provide the conducting interconnections.

In preferred embodiments of this invention, high molecular weight epoxy resins are used. Among the commercially available resins useful in this invention are the following:

(a) Dow Chemical Company, Midland, Michigan Dow (Registered Trade Mark) Epoxy Resin—664 (Diglycidyl ether of epichlorohydrin and bisphenol A-DGEBA), semi-solid, viscosity (Gardner) R-V@25° C, epoxide equivalent weight of 875—975.

(b) Dow Epoxy Resin—667 (DGEBA) semi-solid, viscosity (Gardner) Y-Z (40% in Dowanol (Registered Trade M) DB @ 25° C), epoxide equivalent weight of 1600—2000 and other epoxy resins such as:

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(72) Inventors MICHAEL JAMES CANESTRARO and MICHALE THEODORE ORINIK

(54) AN EPOXY RESIN COMPOSITION

(71) We, INTERNATIONAL BUSINESS MACHINES CORPORATION, a Corporation organized and existing under the laws of the State of New York in the United States of America, of Armonk, New York 10504, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to an epoxy resin composition.

In the preparation of printed circuitry it is often desirable to use a material which can be used as a resist and as a dielectric material as well. For example, in multilayered circuitry it is desirable to be able to form interconnect holes between two levels of circuitry by use of conventional photoresist techniques rather than the drilling operation presently in use and at the same time deposit a dielectric film. Techniques have been developed in which the circuitry is coated with a material which, upon exposure to light, will become soluble to a given solvent in the exposed areas while insoluble in the unexposed areas, i.e. a positive resist material. It is desirable that this material also be a good dielectric material so that a subsequent circuit can be disposed thereon without need of the conventional steps of removing the photoresist material and coating the circuitry board with a dielectric.

While there are a number of commercially available positive photoresist compositions, such as Shipley's AZ-1350, AZ-119, Eastman Kodak KAR-3, none of these materials are found to be suitable dielectric materials in the preparation of printed circuitry.

According to the invention there is provided an epoxy resin composiiton comprising an epoxy resin having an epoxide equivalent weight of from 800 to 2000; an amine curing agent; a halogenated polycarboxylic acid anhydride, and a halogenated hydrocarbon solvent.

It has been discovered that positive photoresist can be prepared from epoxy resins. The resins are dissolved in halogenated hydrocarbons to which is added an amine curing agent and a halogenated anhydride. Preferably the composition includes said epoxy resin from 5% to 30% by weight of the composition, said amine from 2% to 10% by weight of the composition and said halogenated anhydride from 1% to 5% by weight of the composition. The amount of the solvent will vary depending on the desired viscosity, i.e. depending upon the coat thickness desired.

This approach toward making a positive image in a thermosetting dielectric has many applications in the field of electronic circuitry. Besides its use as a protective coat it has great potential use in multilayer circuitry where the photopositive epoxy resist eventually becomes the permanent dielectric. Instead of the conventional mechanical drilling of holes for interconnecting metallic layers, one can use an appropriate mask and "dissolve out" the hole with mild organic solvents, and then follow with conventional electroless and metal plate through techniques to provide the conducting interconnections.

In preferred embodiments of this invention, high molecular weight epoxy resins are used. Among the commercially available resins useful in this invention are the following:

(a) Dow Chemical Company, Midland, Michigan Dow (Registered Trade Mark) Epoxy Resin—664 (Diglycidyl ether of epichlorohydrin and bisphenol A-DGEBA), semisolid, viscosity (Gardner) R-V@25° C, epoxide equivalent weight of 875—975.

(b) Dow Epoxy Resin—667 (DGEBA) semisolid, viscosity (Gardner) Y-Z (40% in Dowanol (Registered Trade M) DB @ 25° C), epoxide equivalent weight of 1600—2000 and other epoxy resins such as:

SEE ERRATA SLIP ATTACHED

1) Other diglycidyl ethers of epichlorohydrin and bisphenol A
2) Polyglycidyl ethers of phenol-formladehyde condensates
3) Diglycidyl ether of resorcinol

The particular amine used as a curing agent can be chosen from any number of amino compounds, such as methylenedianiline, phenylenediamine, diaminodiphenylsulfone, diethylenetriamine, triethylenetetramine. Aromatic amines are preferred. The amine is present in the formulation from 2.0 grams to 10 grams per 100 grams of dry resin.

The solvents used in this invention are selected from the halogenated hydrocarbons. Preferred solvents are chosen among methylene dichloride, chloroform, ethylene dichloride, methylene dibromide, bromoform and ethylene dibromide and mixtures thereof. The amount of solvent used is easily determined to one skilled in the art. It will be dependent upon the desired viscosity and the desired thickness of the coating.

Suitable anhydrides are selected from among the halogenated anhydrides such as chlorendic anhydride, dichloromaleic, tetrabromophthalic, dichlorocitraconic, tetrachlorophthalic and halogenated derivatives of trimellitic, pyromellitic anhydrides. They are added to the epoxy-amine solution in the amounts of from 2.0 grams to about 10.0 grams per 100 grams of dry resin.

A typical formulation is as follows:

PART I

	grams
Epoxy Resin	100
Chloroform	100
Methylene Dichloride	100
Methylene Dianiline	2.5

PART II

Chlorendic Anhydride	5.0

The solution in Part I is found to be stable for long periods of time when refrigerated. Depending on the molecular weight of the epoxy resin, it may be desirable to advance the thermal cure of part I before adding part II, to optimize exposure and further thermal cure before image development. After the addition of the anhydride, the solution is found to be stable for about 3 days.

The viscosity of the solution may be adjusted for proper coating thickness. It may be sprayed, dipped or roller coated.

In the preparation of printed circuitry the epoxy formulation is generally coated onto a copper substrate, air dried, exposed to U.V. light in a predetermined pattern from a 200 watt Hg vapour lamp, at a distance of from 12 inches to 24 inches. The time of exposure is from 3 minutes to 30 minutes, depending on the coating thickness. For example, if the coating is 0.5 mil thick, the exposure time is about 3 minutes and if it is about 3.0 mils, the time exposure is 30 minutes. After U.V. exposure, the coatings are oven baked at 60° C to 80° C for 5 minutes to 1 hour (again depending on the thickness of the coating) to render the unexposed areas of the epoxy coating thermally cured to a state of insolubility. The exposed areas remain soluble and are developed with a suitable solvent as indicated above. Solvent development can vary from 30 seconds to 5 minutes depending on the degree of U.V. exposure and predevelopment cure. The process gives a positive image of good resolution of up to 100 lines/mm.

By way of illustration specific examples for the preparation of a printed circuit board are hereinafter given:

EXAMPLE I

A copper cladded board is dip coated with the following composition:

	grams
DER 667	100
Chloroform	100
Methylene Dichloride	100
Phenylene Diamine	2.5
Chlorendic Anhydride	5.0

The copper cladded card had an epoxy coating thickness of about 1.0 mil. It is then exposed in a predetermined pattern to ultraviolet radiation having a wavelength of about 3500Å or less, for about 3 minutes. The sample is then placed in an oven and heated at 60° C for about 5 minutes, after which a positive image is developed by immersing the same in methylene dichloride. The developed image can then be copper plated by conventional techniques.

EXAMPLE II

A copper cladded board is dip coated with the following composition:

	grams
DER 664	100
Chloroform	100
Methylene Dichloride	100
Phenylene Diamine	2.5
Chlorendic Anhydride	5.0

The so coated card was treated as in Example I and like results were obtained.

EXAMPLE III

Other formulations were tried, using the epoxy materials, amines and halogenated anhydrides listed above. Each of the formulations tried produced positive images much like those provided in Examples I and II.

Although the mechanism of the reaction is not fully understood, it is believed that the chlorendic anhydride interferes with the ther-

mal cure at the U.V. exposed areas. Upon photolysis, chlorendic anhydride may possibly release small amounts of HCl which may form a salt with the amine curing agent, with the amine salt being less reactive towards thermal cure. This results in a differential solubility between U.V. exposed and unexposed areas. Another possibility is a reaction of the epoxide group with HCl or chlorendic anhydride in the photolyzed areas to slow the rate of thermal cure.

WHAT WE CLAIM IS:—

1. An epoxy resin composition comprising an epoxy resin having an epoxide equivalent weight of from 8000 to 2000; an amine curing agent; a halogenated polycarboxylic acid anhydride, and a halogenated hydrocarbon solvent.

2. A composition according to claim 1, wherein said epoxy resin is diglycidyl ether of epichlorohydrin and bisphenol A, polyglycidyl ether of a phenol-formaldehyde condensate, or diglycidyl ether of resorcinol.

3. A composition according to claim 1 or 2, wherein said amine curing agent is methylenedianiline, phenylenediamine, diaminodiphenylsulfone, diethylenetriamine or triethylenetetramine.

4. A composition according to any one of claims 1 to 3, wherein said halogenated anhydride is chlorendic anhydride, dichloromaleic, tetrabromophthalic, tetrachlorophthalic, dichlorocitraconic and halogenated derivatives of trimellitic or pyromellitic anhydrides.

5. A composition according to any one of the preceding claims including said epoxy resin from 5% to 30% by weight of the composition, said halogenated anhydride from 1% to 5% by weight of the composition, and said amine from 2% to 12% by weight of the composition.

6. An epoxy resin composition substantially as hereinbefore described in Example I or II.

7. A method of preparing printed circuit boards including the steps of coating a copper cladded board with a composition claimed in any of the preceding claims, exposing said coating to ultraviolet radiation in a predetermined pattern, heating said coating to cause hardening of the unexposed areas, developing said coating to remove exposed areas of said coating and thereafter metal plating said coating.

8. A method of preparing printed circuit boards according to claim 7 substantially as hereinbefore described.

9. A printed circuit board prepared by a method claimed in claim 7 or 8.

M. S. CHAUDHRY,
Chartered Patent Agent,
Agent for the Applicants.

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